Electronic Supporting Information (ESI)

Tandem redox system with cobalt complex and 2-azaadamante-N-oxyl for fast dye regeneration and exceeding open circuit voltage 1 V

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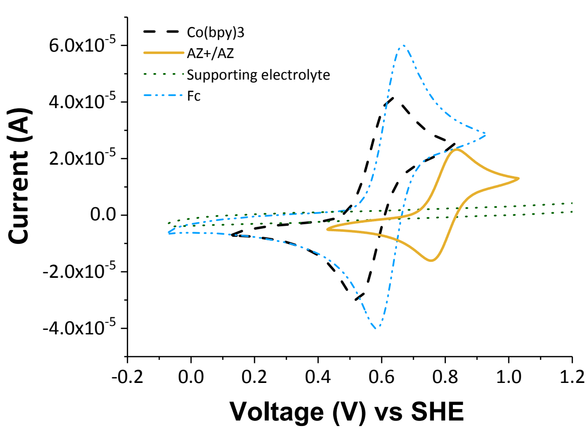
Electrochemical Measurements: Cyclic voltammetry measurements (Fig S.1) were performed with a potentiostat Bio Logic SP300, in a three-electrode setup cell. A glassy carbon electrode served as the working electrode (0.07cm^2 area) and a graphite rod as the counter electrode; a non-aqueous reference electrode of Ag/AgCl (1 M LiCl in ethanol) was used, with an intermediate bridge tube containing the same supporting electrolyte as the working electrode compartment. The electrolyte solutions contained 2 mM of active species, and 0.1 M of LiTFSI as supporting electrolyte in dry acetonitrile. The scan rate was 100 mV s^{-1}, formal potentials were determined vs ferrocenium/ferrocene as a reference system, (0.21 V in our experimental conditions), and then vs SHE (with a value established for Fc^+/Fc = 0.624 V versus SHE in acetonitrile and 25 °C).[1] Cyclic voltammetry measurements to determine the current-potential plots of the symmetrical cells (Fig S.2) were also performed with the Bio Logic SP300 potentiostat. A chronopotentiometry method at zero current (Fig 3) was used to determine the redox potential of a tandem mixture were also performed with the Bio Logic SP300 potentiostat.



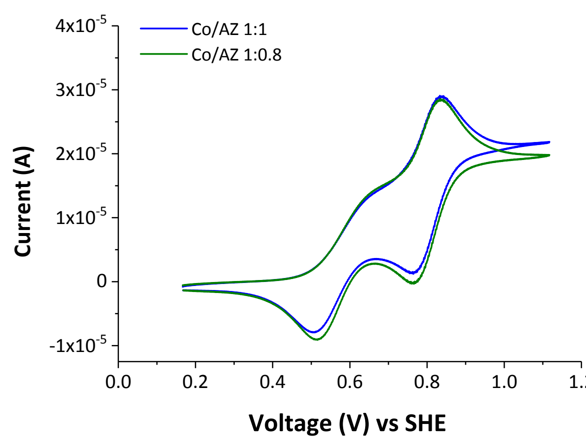


Figure S.1. Cyclic voltammetry with a three-electrode cell with glassy carbon as the working electrode, a graphite rod as the counter electrode, and a non-aqueous reference electrode of Ag/AgCl (2 M in ethanol) and scan rate of 100 mV s^{-1} of (a) AZ 2 mM/AZ+ 0.5 mM and $[Co(bpy)_3]^{2+}$ 2.5 mM/$[Co(bpy)_3]^{3+}$ 0.6 mM, (b) and tandem mixtures Co/AZ 1:1 and Co/AZ 1:0.8.

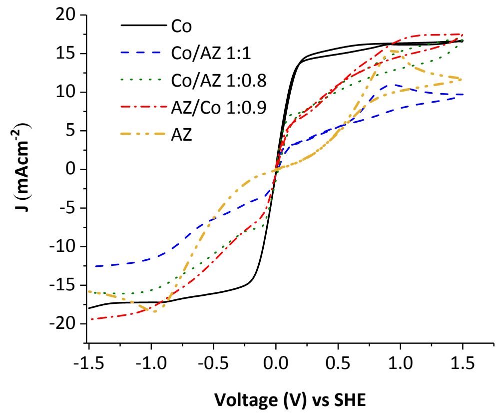


Figure S.2. Current density vs voltage plots for symmetric cells containing the tandem electrolyte systems.

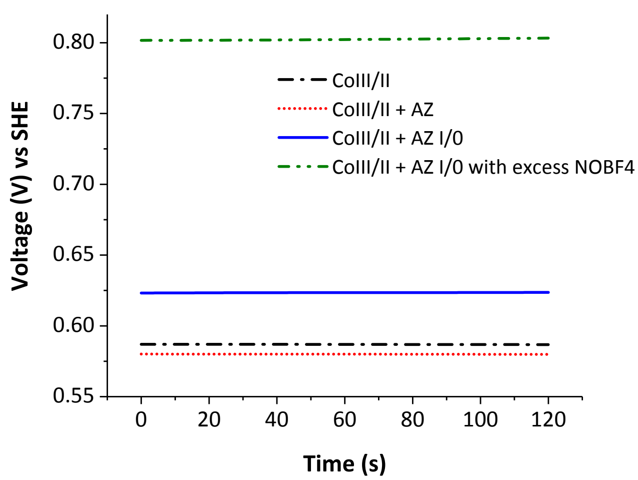
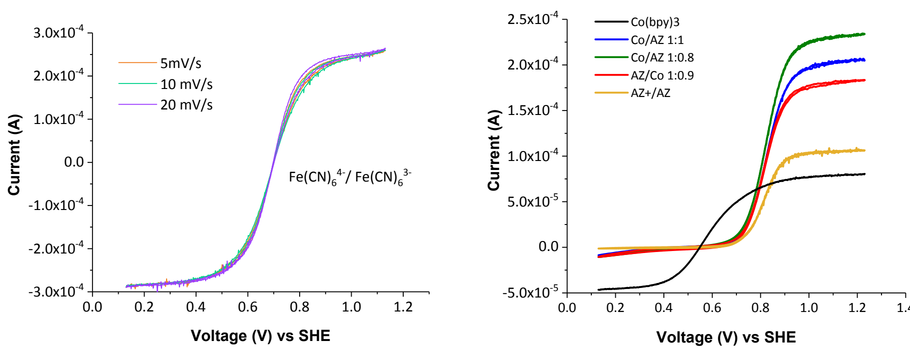


Fig S.3. Plot of voltage vs time in a chronopotentiometry method (zero current) of (a) 2 mM $Co(bpy)_3^{2+}$, 0.5 mM $Co(bpy)_3^{3+}$, 0.1 M LiTFSI (dash-dotted black line), (b) 2 mM $Co(bpy)_3^{2+}$, 0.5 mM $Co(bpy)_3^{3+}$, 0.1 M LiTFSI, 2 mM AZ (dotted red line) and (c) 2 mM $Co(bpy)_3^{2+}$, 0.5 mM $Co(bpy)_3^{3+}$, 0.1 M LiTFSI, 2 mM AZ, 0.1 mM AZ^+ by adding the corresponding amount of $NOBF_4$ (solid blue line), and (d) excess of $NOBF_4$.

Diffusion coefficients measurements:

Current-voltage measurements were performed via rotating disk electrode. A potentiostat/galvanostat AUT 71326 Metrom/Autolab, with a three-electrode set-up with a glassy carbon rotating disk electrode as working electrode and a graphite rod as the counter electrode; a non-aqueous reference electrode of Ag/AgCl (1 M LiCl in ethanol) were used, with an intermediate bridge tube containing the same supporting electrolyte as the working electrode compartment. A water flow at 25 °C was used to keep the cell temperature constant at 25 °C. The rotor speed was controlled by a speed control unit (Radiometer Ananlytical-CVTV101) and set at 1000 rpm for all the experiments. A calibration with an electrolyte of 1 M NaOH, 1.00x10^{-2} M of $Fe(CN)_6^{3-}$ and 1.04x10^{-2} M $Fe(CN)_6^{4-}$ was performed, using the diffusion coefficients of 6.77x10^{-6} cm^{2}s^{-1} and 5.81x10^{-}respectively, as reported by Bazán, et.al.[2] The Levich equation (S.E.1) was used to determine the diffusion coefficients, where i_L is the limiting current (A cm^{-2}), c_i the concentration in mol cm^{-3}, ν the kinematic viscosity in cm^{2}s, ω the rotation rate in rad s^{-1} and D the diffusion coefficient in cm^2 s^{-1}, and the electrode are was determined to be 0.0337 cm^2

$$i_L = \frac{zF}{1.61} c_i \nu^{-1/6} \omega^{1/2} D_i^{2/3} \qquad \text{(SE.1)}$$



(a) (b)

Figure S.4. Current vs voltage plots measured with a rotatory disk electrode (a) calibration with $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4}$ electrolyte and (b) tandem system electrolytes.

Table S.1. Diffusion coefficients of the actives species in acetonitrile, measured with a rotatory disk electrode.

Electrolyte	Active species	Concentration (mM)	Jlim (A/cm2)	D (cm2/s)
$Co(bpy)_3$	**Co(II)**	2.00	3.91± 0.15E-03	7.26±0.42E-06
	Co(III)	0.5	-8±1E-04	1.11±0.22E-05
AZ	**AZ**	2	3.22±0.05E-03	1.54±0.02E-05
	AZ^+	0.4	-4.2±0.2 E-05	1.87±0.1E-07
Co/AZ 1:1	**Co(II)**	2	-	-
	AZ	2	-	-
	Total	4	6.04±0.07E-03	1.39±0.03E-05
	Co(III)	0.5	-2.73±0.1E-04	3.04±0.1E-06
Co/AZ 1:0.8	**Co(II)**	2.4	-	-
	AZ	2	-	-
	Total	4.4	7.48±0.04E-03	1.67±0.01E-05
	Co(III)	0.5	-3.40±0.08E-04	4.22±0.1E-06
AZ/Co 1:0.9	**Co(II)**	1.8	-	-
	AZ	2	-	-
	Total	3.8	5.46±0.05E-03	1.40±0.02E-05

Co(III)	0.4	-3.22±0.4E-04	3.90±0.7E-06

Electrochemical Impedance Measurements (EIS): Impedance measurements were performed using a Bio Logic SP300 potentiostat, over a frequency range from 1 MHz down to 0.1 Hz at 0 V for the symmetrical cells and at bias potentials between 0 and 1.1 V (with a 10 mV sinusoidal AC perturbation) for complete devices under dark conditions. All measurements were done at 20 °C. The resulting impedance spectra were analyzed with Z-view software (v2.8b, Scribner Associates Inc.).

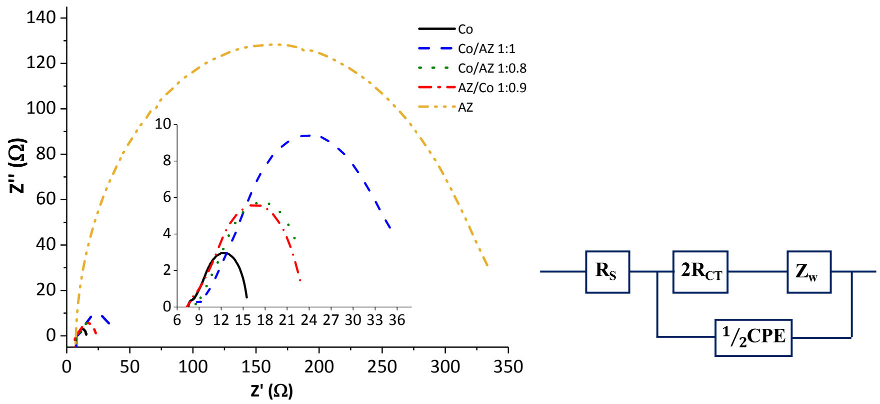


Figure S.5 Nyquist plots for symmetric cells containing the tandem electrolyte systems, at 0 V.

Table S.2. Photovoltaic parameters of DSSC with the dye XY1, PEDOT as CE and different electrolyte systems.

Light intensity	Parameter	Co(III/II) Ref	Co(II)/AZ 1:1	Co(II)/AZ 1:0.8	Co(II)/AZ 0.8:1	AZ+/AZ
0.1 Sun	V_{OC}(mV)	822 ± 20	845 ± 9	856 ± 11	861 ± 12	811 ± 13
	J_{SC}(mAcm^{-2})	1.38 ± 0.09	1.32 ± 0.04	1.34 ± 0.04	1.30 ± 0.05	1.37 ± 0.04
	FF	0.76 ± 0.02	0.73 ± 0.01	0.76 ± 0.03	0.77 ± 0.04	0.73 ± 0.02
	η **(%)**	8.6 ± 0.5	8.2± 0.2	8.4 ± 0.2	8.4 ± 0.1	8.2 ± 0.3
0.5 Sun	V_{OC}(mV)	860 ± 18	952 ± 8	949 ± 12	958 ± 15	863 ± 20
	J_{SC}(mAcm^{-2})	6.9 ± 0.4	6.5 ± 0.3	6.8 ± 0.2	6.8 ± 0.1	5.8 ± 0.4
	FF	0.71 ± 0.01	0.67 ± 0.02	0.71 ± 0.02	0.71± 0.02	0.55 ± 0.06
	η **(%)**	8.1 ± 0.5	8.0 ± 0.6	8.8 ± 0.3	8.7 ± 0.3	5.3 ± 0.5
1 Sun	V_{OC}(mV)	877 ± 17	989 ± 9	988 ± 12	997 ± 19	874 ± 35
	J_{SC}(mAcm^{-2})	12.5 ± 0.8	12.26 ± 0.5	12.8 ± 0.3	12.8 ± 0.3	10.2 ± 0.4
	FF	0.68 ± 0.01	0.64 ± 0.01	0.69 ± 0.02	0.68 ± 0.02	0.56 ± 0.08
	η **(%)**	7.5 ± 0.6	7.7 ± 0.3	8.7 ± 0.3	8.6 ± 0.3	5.2 ± 0.9
# of devices		9	7	9	9	9

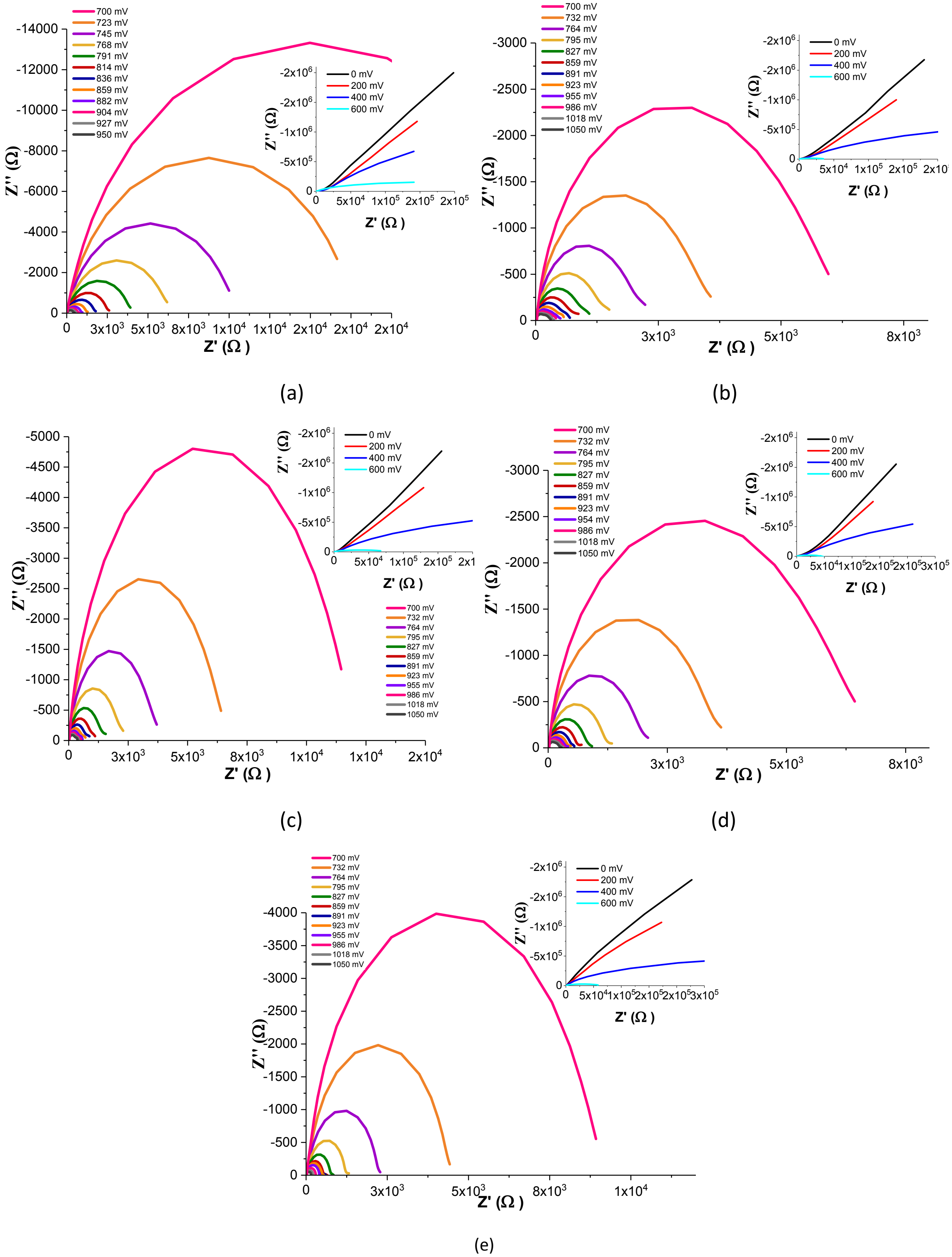
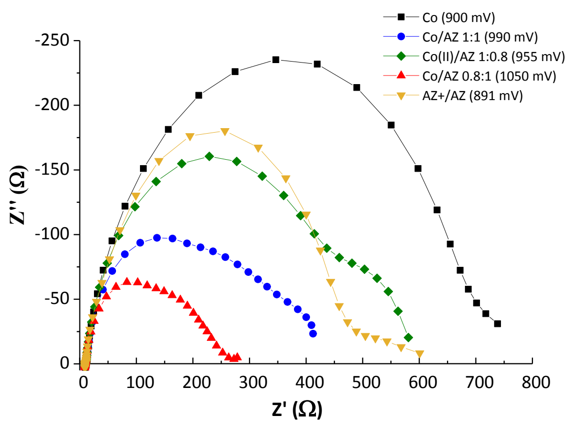
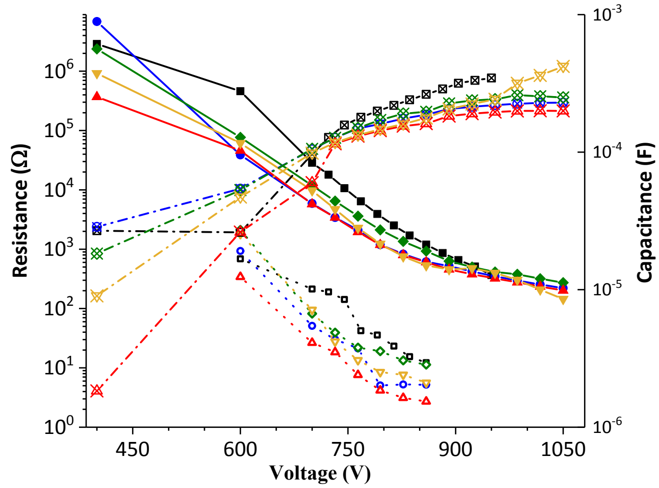


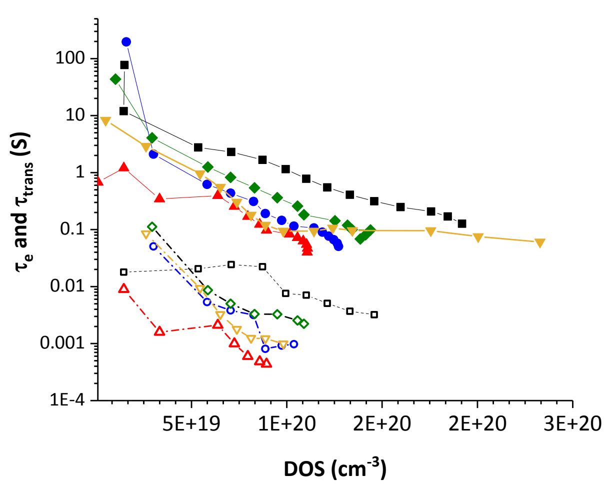
Figure S.6. Nyquist plots under dark conditions for DSSC with electrolytes of a) $[Co(bpy)_3]^{3+/2+}$ reference, b) Co/AZ 1:1, c) Co/AZ 1/0.8, d) AZ/Co 1:0.9 and e) AZ^+/AZ electrolyte.



(a)



(b)



(c)

Figure S.7. EIS analysis. (a) Nyquist plots at open circuit voltage for each electrolyte system, (b) continous lines with solid markers represent the charge transfer resistance R_{CT} as function of applied voltage, the dotted lines with open markers the transport resistance R_{trans}, dasd-dotted lines with and x marker represents capacitance, (c) electron lifetime and transport time vs density of states, DOS. For all the plots the squares correspond to the $[Co(bpy)_3]^{3+/2+}$ reference, the circles to Co/AZ 1:1, diamonds to Co/AZ 1/0.8, triangles to AZ/Co 1:0.9 and inverted triangles to the AZ^+/AZ electrolyte.

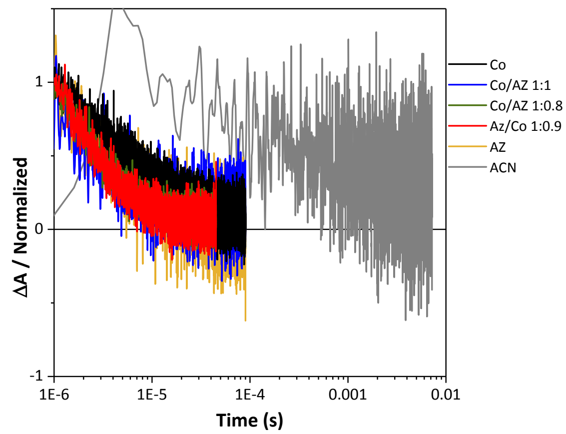


Figure S.8. Transient absorption spectroscopy measurements of DSSC with tandem electrolytes.

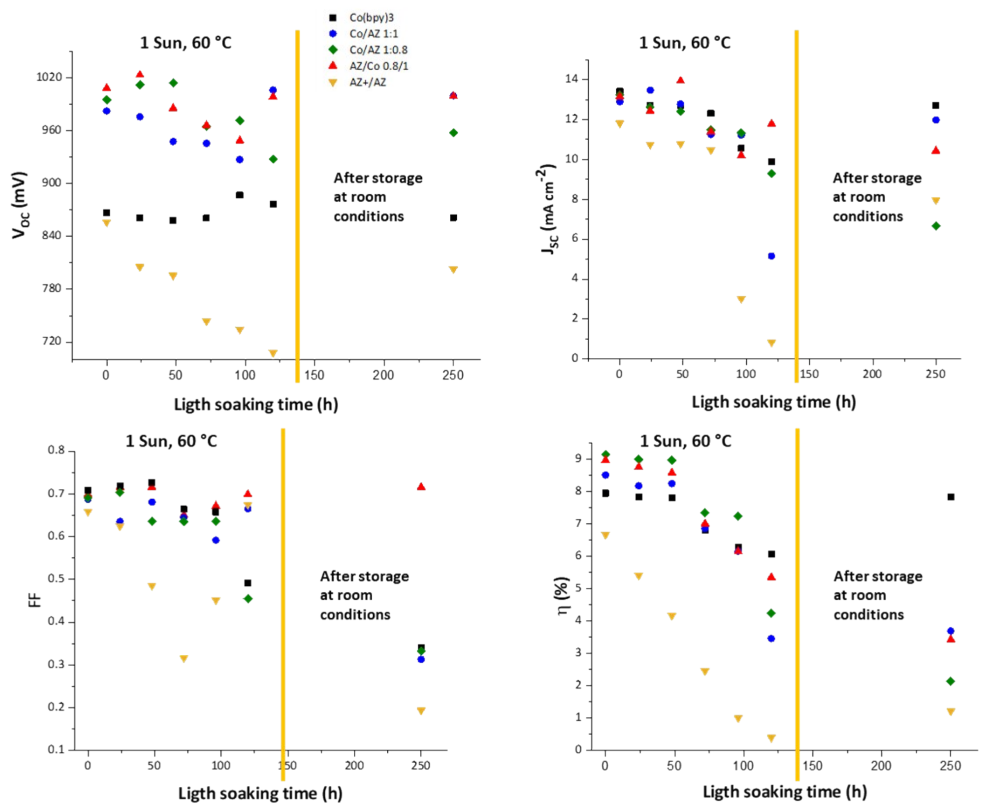


Figure S.9 Photovoltaic parameters of DSSC with the dye XY1, PEDOT as CE and different electrolyte systems in acetonitrile.

References

1 V. V. Pavlishchuk and A. W. Addison, *Inorganica Chim. Acta*, 2000, **298**, 97–102.

2 J. C. Bazàn and A. J. Arvìa, *Electrochim. Acta*, 1965, **10**, 1025–1032.